

DECLARATION

In the matter of
U.S. Serial No. 10/521,453
in the name of Shigeo MARUYAMA,
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I, the undersigned, Hidekatsu KAWASHIMA, of Fujimoto Patent and Law Office, of Room 317, Sanno Grand Building, 14-2, Nagata-cho 2-chome, Chiyoda-ku, Tokyo, Japan, do solemnly and sincerely declare as follows:

1. That I am well acquainted with the English and Japanese languages and am competent to translate Japanese into English and vice versa.

2. That I have executed, with the best of my ability, a true and correct translation to the attached copy of the complete description, claims, drawings and abstract originally filed as Japanese Patent Application No. 2002-208800.

This 13th day of February, 2008


Hidekatsu KAWASHIMA

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[Name of Document] SPECIFICATION

[Title of the Invention] PRODUCTION PROCESS FOR FINE
CARBON FIBER

[Scope of the Claims]

5 [Claim 1] A process for producing a fine carbon fiber
by a method of thermal decomposition (CVD, CCVD) of an
organic compound, in which an ultra fine particle
comprising at least one transition metal is used as a
catalyst, is characterized in that a compound containing
10 at least one VIB group element in the periodic table
and/or a compound containing at least one VIB group
element in the periodic table and at least one organic
compound are reacted under a pressure of 2×10^5 Pa or less.

15 [Claim 2] The process for producing a fine carbon
fiber as described in claim 1, wherein the fine carbon
fiber has a fiber diameter of 0.1 nm or more to 1 μ m or
less.

20 [Claim 3] The process for producing a fine carbon
fiber as described in claim 1, wherein the fine carbon
fiber comprises a single-walled carbon nanotube in which
a fiber diameter is at least 5 nm or less and which has
an axial chiral structure.

25 [Claim 4] The process for producing a fine carbon
fiber as described in claim 1, wherein the fine carbon
fiber comprises a multi-walled carbon nanotube in which a

fiber diameter is at least 10 nm or less and which has an axial chiral structure.

[Claim 5] The process for producing a fine carbon fiber as described in any one of claims 1 to 4, wherein
5 an organic compound containing a VIB group element in the periodic table in a molecule thereof is a compound containing oxygen.

[Claim 6] The process for producing a fine carbon fiber as described in any one of claims 1 to 4, wherein
10 an organic compound containing a VIB group element in the periodic table in a molecule thereof is a compound containing sulfur.

[Claim 7] The process for producing a fine carbon fiber as described in claim 5, wherein the compounds
15 containing oxygen as a VIB group element are CO, CO₂, alcohols, ketons, phenols, ethers, aldehydes, organic acids or esters.

[Claim 8] The process for producing a fine carbon fiber as described in claim 6, wherein the compounds
20 containing sulfur as a VIB group element are H₂S, S, CS₂, SO₂, thiophenes, thioethers and thiophenes.

[Claim 9] The process for producing a fine carbon fiber as described in any one of claims 1 to 8, wherein a catalyst comprising an ultra fine particle of a
25 transition metal is an ultra fine particle of a

transition metal or an ultra fine particle of a compound of a transition metal.

[Claim 10] The process for producing a fine carbon fiber as described in claim 9, wherein the catalyst
5 comprising an ultra fine particle of a transition particle is a catalyst carried on at least one carrier selected from the group consisting of alumina, zeolite, carbon, magnesia and calcia.

[Claim 11] The process for producing a fine carbon
10 fiber as described in any one of claims 1 to 10, wherein after the fine carbon fiber is separated from a gas coming out of a reaction furnace, all or a part of an unreacted VIB group element containing organic compound is recycled into the reaction furnace.

[Claim 12] The process for producing a fine carbon
15 fiber as described in any one of claims 1 to 10, wherein the production is carried out by the production process comprising at least a raw material gas-feeding part, a carrier gas-feeding part, a reaction furnace, a fine
20 carbon fiber-separating and collecting apparatus, a fine carbon fiber tank, a reacted gas-cooling apparatus, and a second fine carbon fiber-separating and collecting apparatus.

[Claim 13] The process for producing a fine carbon
25 fiber as described in any one of claims 1 to 11, wherein

the production is carried out by the production process comprising at least a raw material gas-feeding part, a carrier gas-feeding part, a reaction furnace, a fine carbon fiber-separating and collecting apparatus, a fine carbon fiber tank, a reacted gas-cooling apparatus, a second fine carbon fiber-separating and collecting apparatus and a gas-recycling apparatus.

[Claim 14] The process for producing a fine carbon fiber as described in any one of claims 1 to 11, wherein the production is carried out by the production process comprising at least a raw material gas-feeding part, a carrier gas-feeding part, a reaction furnace, a fine carbon fiber-separating and collecting apparatus, a fine carbon fiber tank, a reacted gas-cooling apparatus, a second fine carbon fiber-separating and collecting apparatus, a gas-recycling apparatus, a second reacted gas-cooling apparatus, a condensate tank and a moisture separator.

[Claim 15] The process for producing a fine carbon fiber as described in any one of claims 1 to 11, wherein the production process comprises at least a raw material gas-feeding part, a carrier gas-feeding part, a reaction furnace, a fine carbon fiber-separating and collecting apparatus, a fine carbon fiber tank, a reacted gas-cooling apparatus, a second fine carbon fiber-separating

and collecting apparatus, a gas-recycling apparatus, a second reacted gas-cooling apparatus, a condensate tank and a moisture separator or an adsorption apparatus.

5 [Claim 16] The process for producing a fine carbon fiber as described in any one of claims 11 to 15, wherein the fine carbon fiber-separating and collecting apparatus comprises a mechanism in which the reacted gas is cooled to 40°C or higher to 150°C or lower and then separated by a filter.

10 [Claim 17] The process for producing a fine carbon fiber as described in any one of claims 14 to 15, wherein the moisture separator uses at least one method of distillation, adsorption and membrane separation.

[Detailed Description of the Invention]

15 [0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to a production process for a fine carbon fiber such as a vapor grown carbon fiber and a carbon nanotube, specifically to a technique for continuously and stably producing a fine carbon fiber at a low cost.

20

[0002]

[Prior Art]

In the field of fine carbon fibers, there has been significant research and focus on carbon nanotubes

25

recently. A carbon nanotube is a vapor grown carbon fiber (VGCF) that is generally referred to by different names depending on the diameter of the fiber. In general, a fiber having a diameter of 1 μm or more is called a vapor grown carbon fiber (VGCF); a fiber having a diameter of 50 nm or less is called a carbon nanotube (CNT); and a fiber having a diameter of larger than 50 nm and smaller than 1 μm is called a carbon nanofiber (CNF).

[0003]

A crystal structure of the above fine carbon materials assumes various forms, including a single-walled carbon nanotube (SWNT) wherein a single layer of a basal plane of carbon is wound into a cylindrical form, a multi-walled carbon nanotube (MWNT) having a structure in which several layers of basal planes are laminated like a concentric circle or an annual ring and a nanocone having a crystal structure falling in the middle of the both described above, that is, a conical structure in which crystal planes spread at a constant angle to a central axis thereof.

[0004]

A fine carbon material of a shape other than a tube includes a ribbon-like fine carbon material having a structure in which basal planes are laminated so that they cross orthogonally against a fiber direction and a

coil-like fine carbon material having an amorphous structure showing no crystallinity.

VGCF, CNF and CNT fine carbon fibers have so far usually been produced by crystallizing carbon from a gas phase by a thermal decomposition method using hydrocarbons and CO in the presence of transition metal catalyst.

[0005]

Initial research in the present field began with studies vapor grown carbon fiber in the 1970s. In the development of initial VGCF, the fibers had a large diameter, and they were produced mainly by a fixed bed method (catalytic chemical vapor deposition method: CCVD method) in which reaction was carried out with a catalyst placed on a substrate or carried on a carrier. However, in an initial fixed bed method of producing VGCF having a relatively large fiber diameter, the fiber was grown at a slow speed and produced in a low reaction yield, and therefore it was difficult to put the method to practical use. However, it was noted that a very fine fiber having a diameter of 50 nm or less could be produced, and it was industrialized by Hyperion Catalyst International Inc. in U.S. in 1990s.

[0006]

On the other hand, a CVD (chemical vapor

deposition) process in which reaction is carried out while allowing a catalyst to fluidize without using a carrier was developed in 1980s, and the yield was notably improved. In 1990s, CNF having a diameter of a level of 100 nm were successfully industrialized (Showa Denko K. K. and Nikkiso Co., Ltd.).

[0007]

It was reported that a carbon nanotube having the finest fiber diameter could readily be produced by an arc process (Nature, 1991 (354), 56 to 58), and since then, there have been ongoing efforts to develop carbon fibers having a smaller fiber diameter. A production process for a single-walled carbon nanotube and a multi-walled carbon nanotube each having a fine fiber diameter of 50 nm or less, particularly 10 nm or less has come to be developed mainly by a process in which a fiber is produced by volatilizing carbon at a very high temperature as is the case with an arc process and a laser process and a CCVD process in which a carbon nanotube is formed on a fixed bed prepared by carrying a catalyst on a conventional ceramic carrier.

[0008]

A carbon nanotube can be used as a filler material for an electron beam source and a composite material which are used for an image display apparatus and a

semiconductor production apparatus, and in this case, it is preferred that the carbon nanotube is crystalline and straight and that it has a fine and even fiber diameter. If the carbon nanotube is not straight, the carbon fibers themselves are liable to be entangled to form flocks. If flocks are formed, they are less liable to be crushed, and it becomes difficult to align the carbon fibers in use. Further, when the carbon fibers are added to a resin and the like as a filler material, they are less liable to be evenly dispersed, so that a composite having the desired characteristics is less likely to be obtained.

[0009]

When an arc process, a laser process or a CVD process is applied in order to produce a carbon nanotube having the characteristics described above, the following problems typically ensure.

In the arc process and the laser process, firstly, the productivity is low since it is difficult to make a large-scale production facility, and it is difficult as well to make a production line continuous. Secondly, in the current arc process, the production efficiency is low since non-fibrous carbon is liable to be produced simultaneously, and it is difficult to separate and collect carbon nanotubes from non-fibrous carbon. Accordingly, it is difficult to produce a carbon nanotube

having high quality suited to industrial products by the arc process and the laser process.

[0010]

On the other hand, the CVD process is the most
5 preferred process for mass production, but it is
difficult to make the fiber diameter small in production
by the CVD process, and the fiber diameter is liable to
be uneven. Further, even if it is possible to make the
fiber diameter small by controlling the production
10 conditions, there used to be the problem that a curled
carbon nanotube is liable to be produced.

[0011]

Of more interest is a CCVD process in which a
carbon nanotube having a fine fiber diameter is produced
15 by using a fixed bed carried thereon with a catalyst.
The production process of a carbon nanotube according to
this CCVD process is almost the same as that of a CCVD
process which had been investigated in the initial stage
of developing VGCF described above, but it is different
20 in that a porous carrier having fine pores such as
zeolite is used as the carrier. Use of such specific
carrier has made it possible to prepare fine catalyst
particles making use of those pores and produce a very
fine carbon nanotube (Kingsuk Mukhopadhyay, Akira Koshino,
25 Toshiki Sugai, Nobuo Tanaka, Hisanori Shinohara, Zoltan

Konya, B. Nagy; Chemical Physics Letters 303 (1997) 117).

[0012]

Fig. 5 is a schematic drawing of a production process for producing a fine carbon fiber by a conventional batch type CCVD process. A production facility 200 shown in this drawing is equipped with a cylindrical reaction furnace 201 placed horizontally, a heater 202 disposed surrounding the periphery of the reaction furnace 201 in order to heat the reaction furnace 201 from the outside, a raw material gas-feeding part 203 and a carrier gas-feeding part 204 which are connected to a right end side of the reaction furnace 201 as shown in the drawing and a catalyst carrier feeding part 205 connected to a left end side of the reaction furnace 201 as shown in the drawing. Further, a first carbon fiber-collecting part 206 for collecting the catalyst carrier which is introduced into the reaction furnace from the catalyst carrier feeding part 205 and used for the reaction together with a fine carbon fiber produced thereon is connected to the right end side of the reaction furnace 201, and a bag filter 208 for receiving a reacted gas from the reaction furnace 201 and separating the reacted gas into the fine carbon fiber and a waste gas is connected to the left end side of the reaction furnace 201.

[0013]

The bag filter 208 is provided with a gas-discharging part 208a and a solid discharging part 208b. A waste gas-treating apparatus 210 and a second carbon
5 fiber collecting part 209 are connected to the gas-discharging part 208a and the solid discharging part 208b described above respectively, and the waste gas separated by the bag filter 208 is discharged into the waste gas-treating apparatus 210, while the fine carbon fiber which
10 is solid is collected in a second carbon fiber-recovering part 209.

[0014]

In the production facility for a fine carbon fiber shown in Fig. 5, the catalyst carrier such as a zeolite
15 carrying catalyst is introduced from the catalyst carrier feeding part 205 into the reaction furnace 201 charged with a raw material gas and a carried gas, and the fine carbon fiber is allowed to grow on the catalyst carrier by thermal decomposition reaction. The catalyst carrier
20 holding the fine carbon fiber on the surface thereof is collected in the first carbon fiber-collecting part 206. Also, the reacted gas after used for the reaction is discharged into the bag filter 208 from the reaction furnace 201, and it is separated into the fine carbon
25 fiber and the waste gas by the bag filter 208. Then, the

fine carbon fiber separated by the bag filter 208 is collected into the second carbon fiber-collecting part 209, and the waste gas is sent to the waste gas-treating apparatus 210. Thus, thus, the fine carbon fiber can be
5 produced by the CCVD process using the production facility shown in Fig. 5.

[0015]

On the other hand, a large amount of a carrier gas (hydrogen, inert gas and the like) has to be introduced
10 into a reaction furnace in producing a vapor grown carbon fiber and a carbon nanotube by the CCVD process and the CVD process described above, and therefore it has been a large factor in increasing the production cost.

[0016]

15 Further, in the production by the CCVD process described above, the remaining unreacted raw material gas, as well as by-products contained in the reacted gas after used for the reaction, can not be discharged to the outside as they are in order to prevent the environment
20 from being polluted. Accordingly, waste gas treatment such as, for example, incineration treatment and adsorption treatment is required for discharging the above gas to the outside. Since a large amount of a carrier gas is used, as described above, in the
25 production by the CCVD process, an amount of the waste

gas itself is increased, and a cost for waste gas treatment grows large.

[0017]

Further, sulfides such as hydrogen sulfide and
5 thiophene are added in some cases for the purpose of
accelerating the carbon fiber producing reaction. In
this case, a sulfur compound is contained in the waste
gas, and therefore it has to be removed. However, an
amount of the waste gas itself is large as described
10 above, so that the treating cost is increased very much.

As described above, the production cost can not
help growing high in the CCVD process because of the
large amounts of the gas used and the waste gas amount.
This is a generally acknowledged problem in mass-
15 producing fine carbon fibers.

[0018]

[Problem to be Solved by the Invention]

An object of the present invention, which has been
made to solve the above problems, is to provide a
20 production process in which a fine carbon fiber such as a
vapor grown carbon fiber and a carbon nanotube, each
having an optional fiber diameter, particularly a fine
fiber diameter, can continuously and stably be produced
at a low cost.

25 [0019]

[Means for Solving Problem]

Investigations by the present inventors to solve the problems described above have resulted in finding that in a process for producing a fine carbon fiber by a thermal decomposition process (CVD process and CCVD process) of an organic compound using ultra fine particles of a transition metal as a catalyst, use of at least one organic compound containing a VIB group element in the periodic table of elements in a molecule as a raw material organic compound makes it possible to produce a fine carbon fiber having high quality and a very fine fiber diameter, and thus the present invention has been completed.

[0020]

Further, use of the above organic compound for the raw material makes it possible to readily separate and recover reaction by-products and the unreacted raw material from the reacted gas, and recycling of the reacted gas into a reaction furnace makes it possible to reduce the amounts of a carrier gas and a waste gas

[0021]

The production process for a fine carbon fiber according to the present invention comprises introducing a raw material gas comprising an organic compound, a carrier gas comprising hydrogen and/or an inert gas and a

catalyst comprising ultra fine particles containing at least one transition metal into a reaction furnace to produce a fine carbon fiber in the reaction furnace described above by thermal decomposition reaction, wherein an organic compound containing a VIB group element in the periodic table of elements is used as the raw material organic compound, and the reaction is carried out at a pressure of 2×10^5 Pa or less. Preferably, at least a part of a reacting gas used for producing the fine carbon fiber, or a gas obtained by removing by-products and unreacted gas from the reacted gas is reintroduced into the reaction furnace by a recycling means connected to the reaction furnace described above and used.

[0022]

Hydrogen gas and other by-products are produced by the decomposition reaction, and they are contained in the gas coming out from the reaction furnace together with the unreacted raw material gas and the carrier gas. If the above by-products are stuck onto the inner wall of the production facility, pipelines and equipments constituting the production facility are likely to be clogged.

[0023]

In the present invention, an organic compound

containing a VIB group element in the periodic table in a molecule is used as the raw material. The VIB group element is preferably oxygen or sulfur, particularly oxygen. For example, when a compound containing oxygen is used, water, CO, CO₂ and hydrogen are produced as by-products.

[0024]

In reference to the organic compound containing a VIB group element in a molecule, the compound containing oxygen includes CO, CO₂, alcohols, ketones, phenols, ethers, aldehydes, organic acids and esters.

To be specific, it includes, for example, methanol, ethanol, propanol, cyclohexanol, acetone, methyl ethyl ketone, acetophenone, cyclohexanone, phenol, cresol, formaldehyde, acetaldehyde, formic acid, acetic acid, propionic acid, oxalic acid, succinic acid, adipic acid, dimethyl ether, diethyl ether, dioxane, methyl acetate and ethyl acetate.

[0025]

The sulfur compound includes H₂S, CS₂, SO₂, S, thiols, thioethers and thiophenes, and thioethers can particularly be used.

The above raw material organic compounds can be fed into the reaction furnace by spraying in the form of gas, liquid, solution or solid.

The above compounds can be used alone or in a mixture of two or more kinds thereof.

[0026]

5 The fine carbon fiber of the present invention is produced by the CVD process or the CCVD process, and ultra fine particles comprising a transition metal are used as the catalyst.

10 The transition metal includes, for example, iron, cobalt, nickel, yttrium, titanium, vanadium, manganese, chromium, copper, niobium, molybdenum, palladium, tungsten and platinum. The compounds thereof also can be used as the catalyst. Further, they may be used alone or in combination of two or more kinds selected from them. The larger catalytic effect is obtained depending on the
15 combination.

[0027]

In respect to the form of the compounds, the metals of single substances, the organic compounds, the inorganic compound or the combination thereof can be used.
20 For example, ferrocene, nickelocene and cobaltocene can be used as the organic compounds. Also, the inorganic compounds may assume any form of oxide, nitrate, sulfate and chloride. Further, in order to raise an efficiency of fiberization, a sulfur compound such as sulfur,
25 thiophene and H_2S may be added when putting the raw

material and the catalyst into the reaction furnace.

[0028]

Further, the catalyst may be fine particles themselves of the metals or the compound described above, and the metals or the compounds described above may be carried on fine particles of an inorganic carrier. For example, alumina, zeolite, carbon, magnesia and calcia can be used as the inorganic carrier.

An introducing method of the catalyst may be any of a method of gasifying alone, a method of gasifying after mixed with the raw material carbon source, a method of diluting with a carrier gas and a method of dissolving in the raw material carbon source and feeding in a liquid form.

In the present invention, carbon having no crystallinity and the VIB group element are reacted by using a transition metal catalyst and a compound containing a VIB group element as the raw material, whereby single-walled and multi-walled carbon nanotubes of a high purity and having a fiber diameter of 10 nm or less and an axial chiral structure can be obtained.

[0029]

According to the preferable production process for the fine carbon fiber of the present invention, the reacted gas used for producing the above-described fine

carbon fiber is re-introduced into the reaction furnace by a recycling means, whereby the reacted gas which has previously been entirely discharged to the outside can effectively be used. This makes it possible to reduce the amounts of carrier gas as well as used and waste gas produced, thereby reducing both production and waste treatment costs. Accordingly, it becomes possible to reduce the production cost of fine carbon fiber via the inventive process as compared with more conventional processes. In particular, the concentration of raw material gas in the reaction furnace has to be maintained at or below a specific dilution level in order to produce a carbon nanotube having a fine fiber diameter of 10 nm or less. This can be effectuated by increasing the amount of the carrier gas, thereby diluting the concentration of the raw material. It is effective to recycle the reacted gas for this purpose.

[0030]

The production process for the fine carbon fiber of the present invention is a process for producing a fine carbon fiber by a thermal decomposition method using a gas containing the VIB group element-containing compound as the raw material and using ultra fine particles of a transition metal as the catalyst. The production process comprises a reaction furnace for allowing a thermal

decomposition reaction therein to produce a fine carbon fiber, a raw material gas-feeding part for feeding a raw material gas into the reaction furnace, a carrier gas-feeding part for feeding a carrier gas into the above-described reaction furnace, a carbon fiber-separating apparatus for separating and collecting the fine carbon fiber produced in the above-described reaction furnace from a reacted gas, an apparatus for condensing and separating condensable components contained in the reacted gas by cooling the gas, and more preferably a recycling means for introducing the reacted gas again into the reaction furnace.

[0031]

In the production of the fine carbon fiber of the present invention, the separating apparatus described above is connected to the carbon fiber-collecting apparatus. The fine carbon fiber separated from the reacted gas by the separating apparatus is collected in the carbon fiber-collecting apparatus. The reacted gas coming out from the separating apparatus is cooled, and then the cooled gas is allowed to pass through another separating apparatus to further collect the fine carbon fiber. The gas coming out from the carbon fiber-collecting apparatus may be directly discharged after waste gas treatment. However, preferably, the gas

remaining after collecting the fine carbon fiber is recycled to the reaction furnace by the recycling means described above. In this case, the above gas is further cooled to condense condensing components such as water produced by the reaction and the unreacted raw material, and then the gas is introduced into the reaction furnace after separating the condensates from it. The separated condensates are subjected to waste liquid treatment and then discharged.

10 [0032]

In such a process, a collecting rate of the fine carbon fiber to a charged amount of the raw material is not reduced by collecting the fine carbon fiber as well from the reacted gas that is cooled after separating the fine carbon fiber from the reacted gas, and an increase in the production cost brought about by reduction in the collecting rate can be prevented.

15 [0033]

The fine carbon fiber produced by thermal decomposition reaction has a very small bulk density and is light, so that the total amount thereof or the carbon fiber peeled from the catalyst floats in the reaction furnace. Accordingly, the reacted gas discharged from the reaction furnace is accompanied with the fine carbon fibers and the reaction by-products. If gas used for

recycling is reintroduced into the reaction furnace as it is mixed with the fine carbon fiber and subjected to the reaction, carbon grows further on the fine carbon fibers to enlarge a fiber diameter (broaden a width of a fiber diameter), so that the desired fiber diameter is not likely to be obtained. Accordingly, the fine carbon fiber contained in the reacted gas is removed in the present invention by providing the separating means described above so that only the gas component is reintroduced into the reaction furnace, whereby the fiber diameter is prevented from becoming large. This makes it possible to stably produce the fine carbon fiber having a desired fiber diameter.

[0034]

Also, if solids such as the fine carbon fiber and high boiling by-products contained in the reacted gas are circulated in the insides of the reaction furnace and the recycling means, they are likely to be stuck on the insides of pipes connecting them, causing clogs. According to the constitution described above, however, the solids such as the fine carbon fiber and the condensate are separated by the separating apparatus, and the gas reintroduced into the reaction furnace does not contain the solids and the condensate. Accordingly, such trouble as described above can be prevented beforehand,

and it becomes possible to stably produce the fine carbon fiber.

[0035]

5 In the production process for the fine carbon fiber of the present invention, a filter, a cyclone and a device obtained by combining them each of which has a function to efficiently separate solids from gas are suitably used as a separating means. The most suited one can be selected from the above filter and cyclone
10 according to an amount and a temperature of the gas.

For example, when an amount of the reacted gas is large, an amount of the fine carbon fiber collected in the separating means becomes large as well, and therefore a load charged on one filter has to be controlled so that
15 it does not become so large. In this case, combination of a filter having a large mesh and a bag filter having a fine mesh or combination of a filter and a cyclone are recommendable.

[0036]

20 The gas coming out from the reaction furnace stays, though depending on a temperature of the reaction furnace, in a high temperature of about 600°C or higher. When using a bag filter, the gas of such a high temperature can not be allowed to pass through it, and therefore
25 separation by the bag filter described above is

preferably carried out after the temperature of the reacted gas is lowered. To be specific, a cooling means such as a water-cooled jacket is provided in a path from the reaction furnace or the carbon fiber-collecting part to the separating apparatus to cool the reacted gas. The gas is cooled down to 40°C or higher to 150°C or lower (preferably 100°C or lower) by the above cooling means, and then separation by the bag filter is carried out. A solid product which is less liable to be cooled is mixed in the reacted gas in a certain case, and therefore it is advisable to use a bag filter which can endure as high temperature as possible for the filter.

[0037]

In the production process for the fine carbon fiber of the present invention, the gas obtained after separating the fine carbon fiber is further cooled to recover the unreacted raw material organic compound and the condensate such as produced water, and they can be separated by an apparatus in which two or more methods of distillation, adsorption and membrane separation are combined.

[0038]

Next, in the production process for the fine carbon fiber of the present invention, when recycling the reacted gas, a temperature of the gas reintroduced into

the reaction furnace is preferably controlled to 40°C or higher.

Substances produced in the above-described reaction furnace are not restricted only to the fine carbon fiber, and the unreacted hydrocarbon and the organic compounds of low boiling point components and high boiling point components are contained as by-products in the reacted gas discharged from the reaction furnace. If the organic compounds are stuck on the inner wall of the production facility, they are likely to clog pipelines constituting the production facility. A measure for preventing these pipelines from being clogged is required in order to safely carry out the production. Various investigations on production conditions therefor repeated by the present inventors have resulted in finding that if a temperature of the gas which passes through at least the recycling means described above and is reintroduced into the reaction furnace is controlled to 40°C or higher, the organic compounds are almost prevented from being deposited and that as a result, the pipelines can be prevented from being clogged. That is, organic compounds can be controlled so that they are not deposited from the raw material gas, the reacted gas and the recycled gas in the facility by controlling a temperature of the gas when passing through the recycling means in which the

temperature of the gas becomes the lowest in the whole of the production facility to 40°C or higher. Accordingly, when the temperature of the gas is lower than 40°C in a position where the temperature of the gas becomes the lowest, the gas is, if necessary, thermally insulated by a means such as covering or heated so that it is maintained at 40°C or higher.

[0039]

Also, the temperature of the gas which passes through the inside of the recycling means described above and is reintroduced into the reaction furnace is more preferably 60°C or higher. That is, if the temperature of the gas is 60°C or higher, the organic compounds can more effectively be inhibited from being deposited from the gas, and therefore further stable production shall be possible.

In respect to a position where the reaction gas described above is reintroduced into the reaction furnace, it may be returned directly to the reaction furnace or may be mixed with the raw material gas and/or the carrier gas and then reintroduced into the reaction furnace. In the case of the latter, for example, in the case where a liquid raw material is gasified for use, the reacted gas is preferably heated to a prescribed temperature in advance so that the raw material gas and the reacted gas

mixed are not liquefied.

[0040]

Next, in the production process for the fine carbon fiber of the present invention, 20 % or more of the reacted gas described above is preferably reintroduced into the reaction furnace by the recycling means and used. Assuming the above constitution makes it possible to obtain a marked cost-reducing effect by reduction in an amount of the carrier gas and an amount of the waste gas. It is more preferably controlled to 50 % or more, but if an organic compound is used for the raw material gas, hydrogen is produced by thermal decomposition reaction, so that an amount of hydrogen contained in the gas coming out from the reaction furnace grows larger than an amount of hydrogen introduced as the carrier gas. Accordingly, the increment of hydrogen due to gas generation has to be discharged. That is, an amount of the gas reintroduced into the reaction furnace for recycling is up to the same amount at the most as that of the carrier gas to be introduced into the reaction furnace.

[0041]

In the production process for the fine carbon fiber of the present invention, the inside of the recycling means described above is preferably a positive pressure to an atmospheric pressure.

In the production process for the fine carbon fiber of the present invention, when reusing the reacted gas by circulating, the reacted gas contains surely hydrogen gas and the raw material organic compound. If oxygen is
5 mixed in the hydrogen gas and the organic compound, a fire and large explosion are likely to be brought about. In order to prevent such an event, the inside of the system in the facility, including the pipelines, has to be maintained at a positive pressure without being a
10 negative pressure. In particular, a suction side of the gas circulating means for circulating the gas in the facility is most liable to cause a negative pressure, and therefore a measure is preferably undertaken so that this part does not become a negative pressure.

15 [0042]

To be specific, the following can be given as the measure for preventing a negative pressure:

(1) increasing a diameter of a pipeline at a suction side of the gas circulating means described above as much as
20 possible,

(2) operating while monitoring a pressure of a suction side of the gas circulating means described above,

(3) controlling so that the facility can be stopped when the pressure becomes a negative pressure,

25 (4) controlling so that a safety gas (for example, inert

gas such as N₂, Ar and the like) can be introduced into the facility when the pressure becomes a negative pressure and

5 (5) constituting the system having a circulating system for controlling pressure before and after the gas circulating means.

[0043]

In the production of the fine carbon fiber of the present invention, a raw material gas fed from a raw
10 material gas-feeding source and a carrier gas fed from a carrier gas-feeding source may be fed separately to the reaction furnace, or may be fed in a mixture of a reaction gas. In the case of the latter, the raw material and the carrier gas are mixed to produce the
15 reaction gas, and the reaction gas is introduced into the reaction furnace.

[0044]

Also, when the reacted gas is recycled, the recycle gas is preferably mixed with the carrier gas and
20 introduced into the reaction furnace.

For example, when an organic compound which is liable to be liquefied is used for the raw material gas, the raw material gas can be prevented from being liquefied by assuming the above constitution, and
25 therefore clogging of the pipelines and an instability in

the raw material concentration can be prevented. Accordingly, the facility can stably be operated, and this makes it possible to enhance homogeneity of the fine carbon fiber produced.

5 Further, an amount of the carrier gas which is newly charged can be reduced, and an amount of the waste gas can be reduced as well, so that both of a carrier gas cost and a waste gas treatment cost can be reduced. Accordingly, the fine carbon fiber can readily be
10 produced at a low cost by means of the CVD process and the CCVD process by using the production facility for the fine carbon fiber of the present invention.

[0045]

[Mode for Carrying Out the Invention]

15 The embodiments of the present invention shall be explained below with reference to the drawings.

[0046]

First embodiment

Fig. 1 is a constitutional drawing schematically
20 showing the production process for the fine carbon fiber showing the first embodiment which is the base of the present invention. The production process of the present invention shown in the above drawing is a production process for producing a fine carbon fiber by the CCVD
25 process, and it is constituted from a cylindrical

reaction furnace 3, a raw material gas-feeding part 2, a carrier gas-feeding part 1 and a catalyst-charging apparatus 20 which are connected to an upper end part of the reaction furnace, a fine carbon fiber-separating and collecting apparatus 4 connected to a lower end part of the reaction furnace 3, a fine carbon fiber-collecting tank 8 connected to a lower part of the fine carbon fiber-separating and collecting apparatus 4, a reacted gas-cooling apparatus 6 connected to an upper part of the same, a separating and collecting apparatus 5 for further separating the fine carbon fiber from a cooled gas and a waste gas-treating apparatus 12.

When producing the fine carbon fiber by the production process shown in Fig. 1, the reaction furnace 3 is first heated and maintained at 600°C or higher to 1250°C or lower by a heater equipped to the reaction furnace 3. The foregoing temperature of the reaction furnace shows one example of the production conditions, and actually, it is set to the optimum condition depending on combination of the kind of a carbon material (an oxygen-containing organic compound and the like) which is used as a raw material, the kind of a catalyst and the kind of a carrier gas.

Next, a raw material gas comprising an organic compound containing a VIB group element is introduced as

a carbon source for a fine carbon fiber into the reaction furnace 3 from the raw material-feeding part 2, and a carrier gas comprising hydrogen, methane or an inert gas is introduced into the reaction furnace 3 from the carrier gas-feeding part 1. Further, a catalyst for causing the reaction of fiberizing carbon in the reaction furnace 3 is introduced into the reaction furnace 3 together with the above gases. Then, the raw material gas is decomposed with heat in the reaction furnace 3, and a fine carbon fiber is produced by the action of the catalyst.

[0047]

Next, the fine carbon fiber produced is sent to the fine carbon fiber-separating and collecting apparatus 4 together with the gas in the reaction furnace. Then, the fine carbon fiber is separated from a reacted gas by the fine carbon fiber-separating and collecting apparatus 4 and sent to the fine carbon fiber tank 8. The gas coming out from the fine carbon fiber-separating and collecting apparatus 4 is cooled to 40°C or higher to 150°C or lower and comes into the second fine carbon fiber-separating and collecting apparatus 5, wherein the fine carbon fiber is further collected by a separating device which can be used for a low temperature gas, such as a bag filter, to be stored in the collecting tank 8. On the other hand,

the gas coming out from the separating apparatus 5 is discharged to the outside of the system after treated by the waste gas-treating apparatus.

[0048]

5 Second embodiment:

Next, the second embodiment of the present invention shall be explained with reference to Fig. 2.

The same elements as the constitutional elements shown in Fig. 1 among constitutional elements shown in
10 Fig. 2 shall be represented with the same symbols, and detailed explanations therefor shall be omitted (the same shall apply to the following examples).

Fig. 2 is a constitutional drawing schematically showing the production process for the fine carbon fiber which is the second embodiment of the present invention.
15 The production process of the present invention shown in the above drawing is a production process for producing a fine carbon fiber by the CCVD process, and it is a process equipped with a recycling apparatus. That is, in
20 the first embodiment described above, the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is discharged to the outside of the system after treated by the waste gas-treating apparatus. However, this is a process in which a part
25 thereof is circulated to the reaction furnace by a gas-

circulating blower 9. In this process, a circulated gas and a discharged gas can freely be controlled, and therefore a gas-circulating amount in the reaction system can readily be controlled.

5 This makes it possible to reduce an amount of a carrier gas made up, and as a result to reduce an amount of a waste gas. Further, the unreacted raw material gas, the VI group element-containing compound and the by-products can be returned to the reaction system, and
10 therefore the yield can be increased.

 Further, the fine carbon fiber is separated at two stages by the separating apparatus 4 and 5, and therefore the fine carbon fiber is not mixed in the circulated gas, so that the fiber can be prevented from becoming thick by
15 allowing carbon to further grow on the fiber.

[0049]

Third embodiment:

 Fig. 3 is a constitutional drawing schematically showing the production process for the fine carbon fiber which is the third embodiment of the present invention. The production process of the present invention shown in the above drawing is a production process in which in the second embodiment described above, a part of the gas coming out from the second fine carbon fiber-separating
20 and collecting apparatus 5 is further cooled by another
25

cooling apparatus 7 which is different from the cooling apparatus 6 before the gas is circulated to the reaction furnace by the gas-circulating blower 9, so that reaction by-products such as water and the non-decomposed raw material organic compound which are contained in the gas are condensed and then separated and removed from the gas to circulate the gas. The condensate separated is sent to a moisture separator 11 via a condensate tank 10 to recover H_2O and an organic compound gas, and this gas is circulated as well to the reaction furnace 3. The condensate stored in the moisture separator 11 is discharged to the outside of the system after treated by a waste water-treating apparatus 15.

In the above process, water and organic compounds having a relatively high boiling point are not contained in the circulated gas, and therefore the moisture concentration is controlled to a lower level. Accordingly, the moisture can be inhibited from being condensed, and the pipelines can be prevented from being clogged.

[0050]

Fourth embodiment:

Fig. 4 is a constitutional drawing schematically showing the production process for the fine carbon fiber which is the fourth embodiment of the present invention.

The third embodiment described above is a process in which only the gas circulated to the reaction furnace by the gas-circulating blower 9 out of the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is cooled by the cooling apparatus 7 to further lower a temperature of the gas, so that the reaction by-products contained in the gas such as water and the non-decomposed raw material organic compound are condensed and then separated and removed from the gas to circulate the gas. However, the production process of the present invention shown in the above drawing is a production process in which the total amount of the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is cooled by the cooling apparatus 7 to separate condensate contained in the above gas. A part of the gas remaining after separating the condensate is circulated to the reaction furnace by the blower 9, and the residual gas is sent to a waste gas-treating apparatus 12 and discharged to the outside of the system after treated. On the other hand, the condensate separated is sent to a moisture separator 11 via a condensate tank 10 to recover H_2O and the organic compound, and this gas is circulated as well to the reaction furnace 3. The condensate stored in the gas-liquid separator 11 is discharged to the outside of the

system after treated by a waste water-treating apparatus
15.

In this process, not only the total amount of the
effective organic compound is recycled, but also water
5 and organic compounds having a relatively high boiling
point are not contained in the circulated gas, and
therefore a moisture concentration in the system is
controlled to a lower level. Accordingly, the moisture
is inhibited from being condensed, and the pipelines are
10 prevented from being clogged. Further, components to be
condensed are not entered into the waste gas-treating
apparatus, and therefore a load charged thereon is
reduced.

[0051]

15 Examples

The present invention shall be explained below in
further details with reference to examples and a
reference example, but the present invention shall by no
means be restricted to the examples described below.

20 [0052]

Example 1

A reaction furnace used is of a structure in which
an SiC-made reaction tube having an inner diameter of 200
 ϕ is heated from the outside, and it is a reaction
25 furnace of a rotary type in which the reaction tube can

be rotated at a constant speed. Ethyl alcohol was used for a raw material of the carbon source and continuously charged at a flow rate of 7.4 NL/minute. Argon was used for a carrier gas, and a flow rate thereof was set to 5 NL/minute. A catalyst prepared by carrying two components of molybdenum and cobalt on magnesium oxide having an average particle diameter of 0.1 μm or less according to a conventional method and then activating it in an inert gas was charged at a rate of 15 g/min. The reaction temperature was set to 810°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 3 rpm.

As a result of the reaction, 19 g/min of crude CNT was obtained, which includes the catalyst and volatile components, and was collected in a CNT-collecting tank. A CNT content in the crude CNT was 3.8 g/min.

[0053]

Example 2

The present example was carried out by the process shown in Fig. 2. Used for a reaction furnace was a reaction tube of a rotary type having a structure in which the same SiC-made reaction tube having an inner diameter of 200 ϕ as in the example 1 was heated from the outside and in which the reaction tube could be rotated

at a constant speed. Ethyl alcohol was used for a raw material of the carbon source as was the case with the example 1, and it was continuously charged at a flow rate of 7.4 NL/minute. A molybdenum and cobalt base catalyst
5 carried on magnesium oxide having an average particle diameter of 0.1 μm or less was activated in an inert gas and then charged at a rate of 15 g/min. The reaction temperature was set to 805°C, and the reaction pressure was set to an atmospheric pressure to continuously carry
10 out the reaction at a rotating speed of 2 rpm. Recycled was the reacted gas (containing unreacted ethyl alcohol and decomposition products) corresponding to 20 % of argon gas contained in the reacted gas at the outlet, and the remaining gas was sent to a waste gas-treating system.
15 Accordingly, the carrier gas in the furnace was argon gas and was controlled so that a newly charged argon gas was 4 NL/min.

As a result of the reaction, the catalyst and crude CNT which were collected in a CNT-collecting tank were
20 19.3 g/min, and a CNT content in the crude CNT was 4.0 g/min. The CNT yield was more improved by 0.2 g/min than the case where recycling was not carried out, and an amount of argon charged was reduced by 20 %.

[0054]

25 Example 3

The present example is a result produced by the process shown in Fig. 3. Used for a reaction furnace in the present example was a reaction tube of a rotary type having a structure in which an SiC-made reaction tube having an inner diameter of 200 ϕ was heated from the outside and in which the reaction tube could be rotated at a constant speed. Ethyl alcohol was used for a raw material of the carbon source as was the case with example 1, and it was continuously charged at a flow rate of 7.4 NL/minute. A molybdenum and cobalt base catalyst carried on magnesium oxide having an average particle diameter of 0.1 μm or less was activated in an inert gas and then charged at a rate of 15 g/min. The reaction temperature was set to 815°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 1 rpm. The reacted gas corresponding to 50 % of argon gas contained in the reacted gas at the outlet was recycled to the reaction system after cooled by a cooler 7 to remove water by a moisture separator 11. Then, the remaining gas was sent to a waste gas-treating system. The carrier gas in the furnace comprised 3 NL/min as a newly charged portion and 3 NL/min as a recycled portion.

As a result of the reaction, the catalyst and crude CNT which were collected in a CNT-collecting tank were

19.6 g/min, and a CNT content in the crude CNT was 4.2 g/min. The CNT yield was more improved by 0.4 g/min than the case where recycling was not carried out, and an amount of argon charged was reduced by 50 %.

5 [0055]

Example 4

The present example is a result produced by the process shown in Fig. 4. Used for a reaction furnace in the present example was a reaction tube of a rotary type having a structure in which an SiC-made reaction tube having an inner diameter of 200 ϕ was heated from the outside and in which the reaction tube could be rotated at a constant speed. Ethyl alcohol was used for a raw material of the hydrocarbon as was the case with example 1, and it was continuously charged at a flow rate of 7.4 NL/minute. A molybdenum and cobalt base catalyst carried on magnesium oxide having an average particle diameter of 0.1 μm or less was activated in an inert gas and then charged at a rate of 15 g/min. The reaction temperature was set to 800°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 1 rpm. The total amount of the reacted gas was cooled in a cooler 7 to recover unreacted components and oxygen-containing hydrocarbons and then recycled to the reaction system after moisture

10

15

20

25

was removed by a moisture separator 11. The reacted gas corresponding to 50 % of argon gas contained in the reacted gas at the outlet of a cooler 7 was recycled, and the remaining gas was sent to a waste gas-treating system. 5 The carrier gas in the furnace comprised 3 NL/min as a newly charged portion and 3 NL/min as a recycled portion.

As a result of the reaction, the catalyst and crude CNT which were collected in a CNT-collecting tank were 19.6 g/min, and a CNT content in the crude CNT was 4.7 10 g/min. The CNT yield was more improved by 0.7 g/min than the case where recycling was not carried out, and an amount of argon charged was reduced by 50 %.

[0056]

[Effect of the Invention]

15 According to the present invention, a fine carbon fiber can continuously and stably be produced at a high yield and a low cost.

[Brief Description of the Drawings]

[Fig. 1] is a constitutional drawing schematically 20 showing the production process for the first embodiment.

[Fig. 2] is a constitutional drawing schematically showing the production process for the second embodiment.

[Fig. 3] is a constitutional drawing schematically showing the production process for the third embodiment.

25 [Fig. 4] is a constitutional drawing schematically

showing the production process for the fourth embodiment.

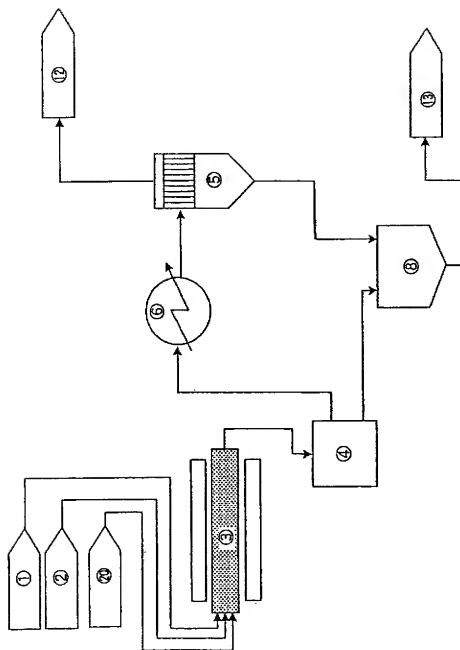
[Fig. 5] is a constitutional drawing schematically showing the production process by a conventional batch type CCVD process.

5 [Explanations of Letters or Numerals]

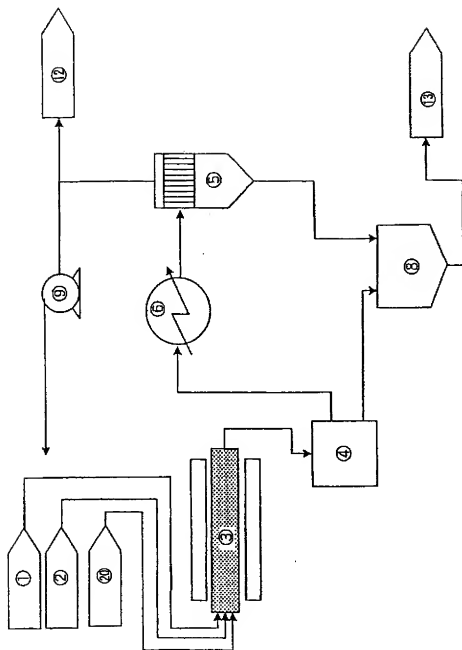
1. Carrier Gas
2. Raw Material Gas
3. Reaction Furnace
4. Fine Carbon Fiber-Separating and Collecting Apparatus
- 10 5. Fine Carbon Fiber-Separating and Collecting Apparatus
6. Cooling Apparatus
7. Condensing Apparatus
8. Fine Carbon Fiber-Collecting Apparatus
9. Gas Cycling Apparatus
- 15 10. Condensate Tank
11. Moisture Separator
12. Exhaust Gas Processing System
13. Rough Fine Carbon Fiber
14. Adsorption Apparatus
- 20 15. Waste Water Processing System
20. Catalyst

[Name of Document] DRAWING

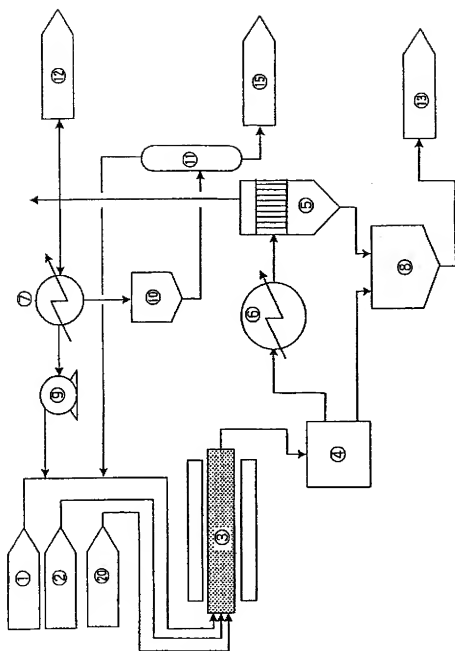
[Fig. 1]



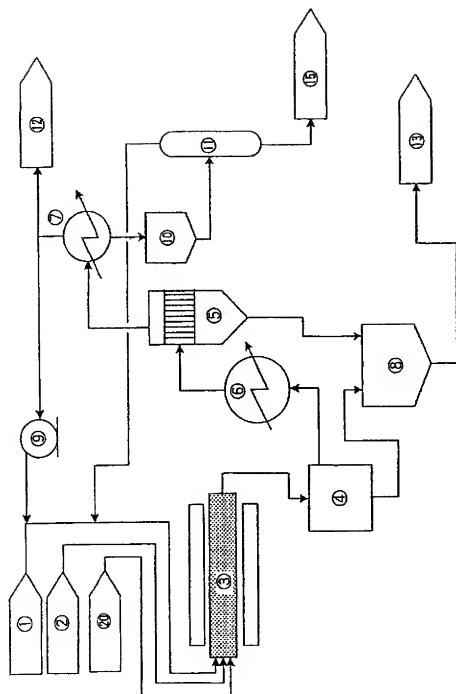
[Fog. 2]



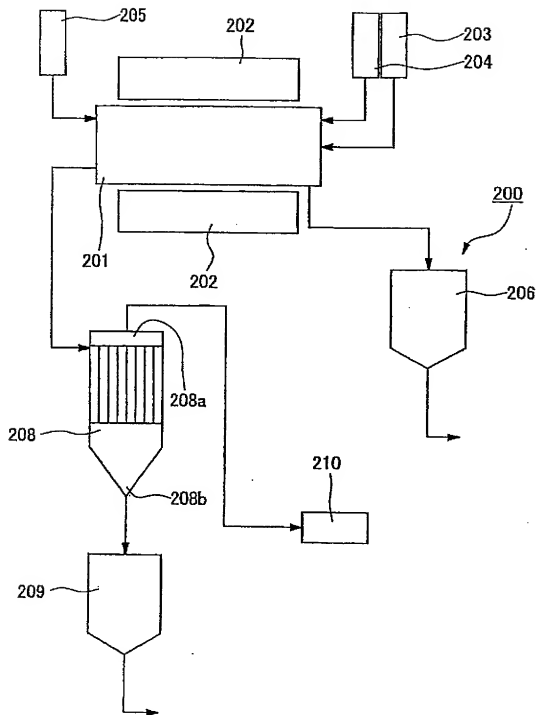
[Fig. 3]



[Fig. 4]



[Fig. 5]



[Name of Document] ABSTRACT

[Abstract]

[Problem] To provide a process for producing continuously and stably a fine carbon fiber having a fine fiber diameter at a low cost.

[Means for Solving Problem] Provided is a process for producing a fine carbon fiber by a method of thermally decomposing a compound containing at least one VIB group element in the periodic table and/or a compound containing at least one VIB group element in the periodic table and at least one organic compound under a pressure of 2×10^5 Pa or less, using an ultra fine particle comprising at least one transition metal as a catalyst. A part or all of a gas coming out of the reaction furnace from which the fine carbon fiber is separated is recycled to the reaction furnace.

[Selected Drawing] Fig. 2